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(21) International Application Number: PCT/US91/07480 (22) International Filing Date: 10 October 1991 (10.10.91) (30) Priority data: 595,037 10 October 1990 (10.10.90) US 769,948 30 September 1991 (30.09.91) US (71) Applicant: BOSTON ADVANCED TECHNOLOGIES, INC. [US/US]; 656 Beacon Street, Boston, MA 02215 (US). (72) Inventor: CLARKE, Richard, H. ; 55 Collier Road, P.O. Box 354, Scituate, MA 02066 (US). (74) Agents: ENGELLENER, Thomas, J. et al.; Lahive & Cockfield, 60 State Street, Boston, MA 02109 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHODS AND SENSOR SYSTEMS FOR SENSING HYDROCARBON-CONTAINING FLUIDS BASED ON FLUORESCENCE DETECTION (57) Abstract <p>Sensors are disclosed for detection of fluorescence as a measure of gasoline or oil leakage. The sensors can be of simple construction and can be buried around the perimeter of a gas station or storage tank. The sensors are based on the principle that gasoline and oils contain additives which can be excited to fluoresce by an inexpensive laser diode, and the fluorescence can be readily detected by a photodetector if the leak has its source in the tank or line, and remain unchanged, if the signal is from a spurious, external source, such as a surface spill which percolates down into the ground or, more commonly, if the ground is already contaminated with fuels from previous leaks or leakage from adjacent sites.</p>		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

METHODS AND SENSOR SYSTEMS
FOR SENSING HYDROCARBON-CONTAINING FLUIDS
5 BASED ON FLUORESCENCE DETECTION

Background of the Invention

The present invention relates to sensors and
10 sensor systems for detection of hydrocarbon-based
fluids, such as leak detectors for fuel storage tanks
and the like.

The detection and measurement of ground
15 water contaminants is of considerable present
interest. It is of particular interest to monitor
the integrity of tanks containing potential
environmental pollutants. For example, gasoline and
oil tanks can cause severe contamination of the local
20 environment, if such tanks begin to leak.

Since it is usually impractical to conduct a
manual or visual inspection of a buried storage tank,
various sensing systems have been devised. For
25 example, bore holes can be drilled and physical
ground water samples taken for off-site chemical
analysis. However, such sampling is time-consuming
and expensive. Moreover, because physical sampling
is only a periodic action, it is unlikely to detect a
30 leak or spill until after significant damage has
occurred.

Various instruments have also been proposed for non-physical and, in some instances, continuous monitoring of ground water and the like based on measurements, for example, of changes in dielectric properties or infrared spectral analysis. However, these systems are typically very expensive and prone to maintenance problems.

It is an object of the present invention to provide improved, non-physical sensors and methods capable of either periodic or continuous monitoring for ground water contamination.

In addition, there is need for sensor systems that can distinguish between ground water contamination due to surface spills which migrate into the ground, on one hand, and actual storage tank, pipe or valve leaks, on the other. This is especially important in gas station and underground tank farm applications where precise identification of the source of contamination can alleviate or reduce the extent of unnecessary excavation.

It is, therefore, another object of the present invention to provide systems for confirming the nature of ground water contamination and/or localizing the source.

It is yet another object of the present invention to provide inexpensive, robust and compact sensors which can be placed, for example, in a conventional bore hole surrounding a fuel tank or other storage depot for hydrocarbon fuels.

Summary of the Invention

The present invention provides methods and sensors for sensing hydrocarbon-based fluids in an ambient environment based on detection of fluorescent additives in such fluids.

One aspect of the present invention is based on a recognition that the additives and dyes used in finished, hydrocarbon-based fluids, such as gasolines, heating oils, motor oils, and other lubricant fluids, exhibit fluorescence under visible light excitation, particularly at 380 nm - 440 nm. Such additives include colored dyes, antioxidants, fuel deicing compounds, metal deactivating agents, anti-static agents, and octane boosting agents, for example. This fluorescence provides a very useful parameter for a contamination detection/monitoring system, especially at very low levels (ppm) of concentration.

In another aspect of the invention, methods and systems are disclosed for confirming leakage from a specific fuel storage tank or other remote site following an initial alarm or other triggering event. In this approach, a highly fluorescent dye is mixed with the contents of a suspect tank or line, and then measurements with the remote sensor or sensors are repeated to ascertain whether the fluorescent dye has entered the sample chamber of a particular sensor. By employing a plurality of such sensors, the location of the leak can be more readily identified.

One particular class of dyes useful for such detection and confirmation of leaks is the Coumarin family which is soluble in gasoline, does not interfere with fuel combustion at the concentrations used (e.g., from about 10^{-4} to about 10^{-8} Molar) and which can fluoresce brightly at a wavelength (i.e., about 530 nm) distinct from the excitation light (e.g., 400 nm - 450 nm).

10 A variety of sensor structures are disclosed. For example, the sensors can include a sample chamber defined within a housing, and in fluid communication with an environment where testing or monitoring is desired (e.g., a bore hole, a tank wall
15 surface, pump, pipe joint or the like). A visible light source is incorporated into, or otherwise coupled to, the housing for irradiation of a fluid sample within the chamber. A fluorescence detector is likewise coupled to the housing for detection of
20 fluorescence or fluorescent components of the fluid sample as irradiated by the light source where the fluorescence is indicative of the presence of a hydrocarbon-based fluid in the environment.

25 The sensors can further include a sample-capturing means to attract fluids in the ambient environment. This sample-capturing means can include, for example, an absorptive material which is permanently or detachably incorporated into the
30 housing of a sensor to imbibe fluids from the environment. The sensor housing can be constructed to include a cavity to receive at least a portion of the absorptive material. Detachable and replaceable absorptive inserts are particularly useful when the
35 sensor is disposed in a bore hole or other remote but

retrievable location, such that, after contamination, the absorptive element can be discarded and replaced so that the sensor may be reused.

5 Preferably, the absorption element includes a porous or semipermeable, hydrophobic polymer, such as polytetrafluoroethylene, polyvinylchloride, polyethylene, polyamides, polymethyl methacrylate, polypropylene, polyethylene terephthalate, or mixtures
10 thereof. These polymers can provide a "wicking" action which draws hydrocarbon-based fluids into the sample chamber.

It is usually desirable that the sensors
15 operate in the visible light range in order to facilitate use of inexpensive flash lamps or light emitting diodes as the light sources and similarly inexpensive photodiodes or the like as the detectors which are operable in the visible light range.
20 Moreover, the use of detectors keyed to a wavelength band ranging from about 380 nm to 440 nm has also been found to minimize interference (e.g., artifacts and masking effects) due to water which typically will also be present in the ambient environment.

25 In a further embodiment of the invention, sensor systems are disclosed in which a plurality of sensors are disposed at various locations around an underground storage tank or underground fuel
30 distribution system. For example, the sensors can be disposed at each pipe joint in an underground pipe or at various locations or interstitial points in an underground tank, as well as in proximity to other structures, such as valves and pumps, where fuel leaks
35 may occur.

When such systems are used, they permit leaks to be readily located, by determining which sensors detect fluorescence in their sample chambers. Such systems also permit verification that
5 the sensor has been triggered by an actual tank leak and not by a false signal. In one verification technique, a strongly fluorescent dye is added to the tank or fuel supply line that has triggered the optical sensor. The fluorescence signal will be
10 enhanced if the leak has its source in the tank or line and remain unchanged, if the signal is from a spurious, external source, such as a surface spill which percolates down into the ground or, more commonly, if the ground is already contaminated with
15 fuels from previous leaks or leakage from adjacent sites.

The invention will next be described in connection with certain illustrated embodiments;
20 however, it should be clear that those skilled in the art can make various modifications, additions and subtractions without departing from the spirit or scope of the invention. For example, although the invention is specifically described in connection
25 with the monitoring of fuel leaks in ground water, it should be clear that the invention is applicable to detection of other types of leaks, and other types of contaminants, as well as monitoring of other types of media.

Brief Description of the Drawings

These and other features and advantages of the present invention will be more fully understood by reference to the following detailed description in conjunction with the attached drawings in which like reference numerals refer to like elements and in which:

FIG. 1 is a schematic block diagram of a 10 sensor system according to the invention;

FIG. 2 is a cross-sectional side view of a sensor according to the invention;

15 FIG. 3 is a cross-sectional side view of another sensor according to the invention;

FIG. 4 is a cross-sectional side view of yet another sensor according to the invention;

20

FIG. 5 is a schematic block diagram of a more comprehensive sensor system according to the invention;

25 FIG. 6 is graph of detected light versus wavelength for a gasoline sample subjected to fluorescence-inducing irradiation according to the invention; and

30 FIG. 7 is a graph of detected light versus wavelength for a fluorescent tag (Coumarin 153) in a gasoline sample which has been likewise subjected to fluorescence-inducing irradiation according to the invention.

35

Detailed Description

In FIG. 1, a system 10 according to the invention is shown, including controller 12, display/alarm unit 14, and sensor 16. The sensor 16 further includes an irradiation source 18 and a detector 20 disposed within a housing 24 having at least one cavity 22 in fluid communication with the ambient environment.

10

In use, controller 12 causes the irradiation source 18 to illuminate the cavity 22. If a hydrocarbon fluid is present in the cavity 22, fluorescence will be detected by detector 20 and an appropriate signal sent back to the controller 12, which then can activate the display or alarm unit 14.

In FIG. 2, a more specific embodiment of the sensor 16A is shown, including a housing 24, surrounded by a flotation collar 32 which permits the disposal of the sensor in a bore hole or other liquid environment. The housing 24 includes an irradiation source 18A (e.g., a light emitting diode) available from various commercial sources, including, LEDtronics, New Jersey) and a detector element 20 (e.g., a conventional photodiode detector). Also shown in FIG. 2 is a hydrocarbon absorption means 26 which is disposed within a cavity of the housing 24 and in fluid communication with the ambient environment. The absorption means can be a porous or semipermeable, hydrophobic polymer (e.g., a polytetrafluoroethylene polymeric sheet of about 1-2 mils thickness), or other matrix material suitable for attracting and retaining hydrocarbon molecules.

Also shown in FIG. 2 is a transmissive filter element 28 (e.g., a glass window with an appropriate anti-reflection coating) and a detector filter 30 (e.g., likewise, a glass element with anti-reflection coating). In use, the filter elements cooperate to improve the efficiency of the sensor. Transmission filter 28 serves as a low pass filter in transmitting only a band of wavelengths from the LED 18A. For example, the transmission filter 28 can selectively transmit wavelengths below about 450 nm, and preferably below about 420 nm in some instances. The detector filter serves as a high pass filter, effectively screening out the excitation wavelength and transmitting to detector 20 only longer wavelength fluorescent light (e.g., above 420 nm and in some instances above 450 nm).

In FIG. 3, another embodiment of a sensor 16B according to the invention is shown, again including a housing 24 and a flotation collar 32 for disposal in a fluid environment. In this instance, the illumination source comprises a fiber optic cable 18B and a lens 19 which illuminate the absorption means 26. Transmission filter 28 and detector filter 30 again cooperate to limit the excitation wavelength and transmit only longer fluorescent wavelengths to the detector 20.

In FIG. 4, another embodiment of a sensor 16C according to the invention is shown, again including a housing 24 and a floatation collar 32 for disposal in a fluid environment. In this embodiment, irradiation source 18 and detector 20 are situated adjacent to each other on one side of the absorption

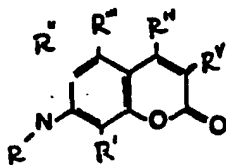
means 26, and a reflective element or surface coating 34 is disposed on the other side of absorption means 26, such that the detector can sense both direct and reflected fluorescence. Again, filter elements 28 5 and 30 are disposed in front of the light source 18 and detector 20 to enhance the optical measurements, as described above.

In FIG. 5 a more comprehensive sensor system 10 40 is shown, including controller 42, display/alarm unit 44, and a plurality of sensors to monitor the integrity of tank 43 and associated elements (e.g., pump 45, vent 47, underground piping 49 and monitoring well 31). These sensors can include bore 15 hole or monitoring well sensors 46 to monitor ground water contamination, as well as other sensors, such as interstitial tank wall sensors 48, vent sensor 50, pump sensor 52, and pipe joint sensors 54, all of which can be similar in design to those described 20 above in connection with FIGS. 2-4.

In FIG. 6, a graph is shown of detected light versus wavelength for a gasoline sample (Exxon 94 octane gasoline) subjected to 25 fluorescence-inducing irradiation according to the invention. The gasoline sample was subjected to excitation light from a laser diode at a wavelength of about 400 nm, producing a sharp fluorescent response at a wavelength of about 425 nm. This 30 fluorescent response is readily detectable by the sensors of the present invention and can, therefore, be used as an indicator of the presence of hydrocarbon pollution in the environment when a sensor detects the fluorescence.

The systems of the present invention can be used not only to monitor the environment surrounding a hydrocarbon fluid storage facility, but also to verify the origin of leaks. When a potential leak is identified, a strongly fluorescent dye is added to the tank or fuel supply line that has triggered the optical sensor. The fluorescence signal will be enhanced, if the leak has its source in the tank or line, and remain unchanged, if the signal is from a spurious, external source.

One particularly useful family of dyes for verification purposes according to the present invention is the Coumarin family of dyes, described generally by the chemical formula:

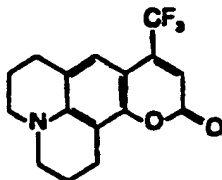


where R in each instance can be the same or different, and denotes either hydrogen or an organic moiety (e.g., lower alkyl, or aryl, or halocarbon groups). Such dyes are commercially available from a variety of sources, including Eastman Kodak of Rochester, New York.

One particularly useful agent is Coumarin 153, commercially available from various sources. The chemical formula for Coumarin 153 is :

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10



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Coumarin 153 has a light absorption maximum (in ethanol) at 423 nm and exhibits a fluorescence max (in ethanol) at 532 nm. FIG. 7 is a graph of detected light versus wavelength for a gasoline sample containing Coumarin 153 and subjected to fluorescence-inducing irradiation according to the invention. The Coumarin-tagged sample was subjected to excitation light from a laser diode at a wavelength of about 400 nm, producing a strong fluorescent response at a wavelength of about 480 nm. This fluorescent response is readily detectable by the sensors of the present invention and can, therefore, be used to verify the source of hydrocarbon pollution in the environment when a sensor detects the fluorescence.

30

Moreover, the presence of the verification agent can be detected simply by measuring the increased intensity of fluorescence in a broad band of the spectrum without measuring the precise wavelength.

As an example to the effect, Coumarin 153 was added at a concentration of $1.55 \times 10^{-4} \text{g}$ in 50 ml of a gasoline sample. Adding a drop of untreated gasoline to the sensor element produced an output (fluorescent) signal of 4.5 volts at the detector; when an additional drop of the gasoline treated with Coumarin 153 at a concentration described above (about 10^{-5}M), the detector output signal increased to 6.5 volts, about a 50% increase and clearly measurable as a verifier of the presence of treated gasoline.

The coumarin dyes are capable of providing the additional fluorescence signal at a trace concentration level of 10^{-5}M (about 125 grams of dye material in a 10,000 gallon tank) and will produce insignificant interference with the stained fuel performance. The verification agent can be produced as a powder or pellet and supplied with the sensor equipment. The pellet can then be premixed with about a gallon of gasoline, dumped into the tank and within a few minutes will diffuse throughout the tank to the leakage point and provide the increased signal signifying verification of the leak.

Nevertheless, it will be understood that the above description pertains to only several embodiments of the present invention. That is, the description is provided by way of illustration and not by way of limitation. The invention, therefore, is to be defined according to the following claims.

What is claimed is:

Claims

1. A sensor for sensing
hydrocarbon-containing fluids in an ambient
5 environment based on detection of fluorescent
additives in such hydrocarbons, the sensor comprising:
a sample chamber;
irradiation means for irradiating a
sample from the ambient environment within the sample
10 chamber; and
detection means for detecting
fluorescence exhibited by the irradiated sample.
2. The sensor of claim 1 wherein the sensor
15 further comprises:
an absorption means disposed within the
sample chamber for absorbing hydrocarbons from said
environment.
- 20 3. The sensor of claim 2 wherein said
absorption means comprises a hydrophobic polymer
material.
- 25 4. The sensor of claim 3 wherein said
material comprises a porous polytetrafluoroethylene
material.
5. The sensor of claim 2 wherein an optical
low pass filter is disposed between the irradiation
20 means and the sample chamber.
6. The sensor of claim 5 wherein said first
plate is selectively transmissive of wavelengths
shorter than about 450 nm.

7. The sensor of claim 5 wherein the filter is coated with an anti-reflection coating.

8. The sensor of claim 2 wherein an optical high pass filter is disposed between the sample chamber and the detector means.

9. The sensor of claim 8 wherein said second plate is selectively transmissive of 10 wavelengths longer than about 420 nm.

10. The sensor of claim 8 wherein the filter is coated with an anti-reflection coatings.

15 11. The sensor of claim 1 further comprising a flotation collar.

12. The sensor of claim 1 wherein said irradiation means comprises a light emitting diode.
20

13. The sensor of claim 1 wherein said irradiation means comprises a flash lamp.

14. The sensor of claim 1 wherein said 25 detection means comprises a photodiode.

15. The sensor of claim 2 wherein the absorption means comprises a polymeric film, and the irradiation means and the detection means are disposed on opposite sides of said absorption means, 5 such that the irradiation means transmits radiation into one side of the film and the detection means detects fluorescence from the other side of the film.

16. The sensor of claim 2 wherein the 10 absorption means comprises a polymeric film deposited on a reflective substrate, and the irradiation means and the detection means are both disposed adjacent to each other on the same side of the film to transmit radiation and detect fluorescence, respectively.

15

17. A sensor system comprising a plurality of sensors at various locations in a fuel storage facility, the system characterized by wherein the sensors comprise:

20

a sample chamber;

irradiation means for irradiating a sample from the ambient environment within the sample chamber; and

detection means for detecting 25 fluorescence exhibited by the irradiated sample.

18. A method for confirming a leak from a hydrocarbon-containing fluid source, the method comprising:

30

mixing a fluorescent dye with the fluid source and then measuring fluorescence at a remote sensor to determine that the dye has migrated with the hydrocarbon-containing fluid due to the leak.

19. The method of claim 18 wherein the method further comprises disposing a plurality of fluorescence-measuring sensors at various locations near the fluid source in order to locate the leak.

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20. The method of claim 18 where the step of mixing a fluorescent dye further comprises mixing a Coumarin dye with the fluid source.

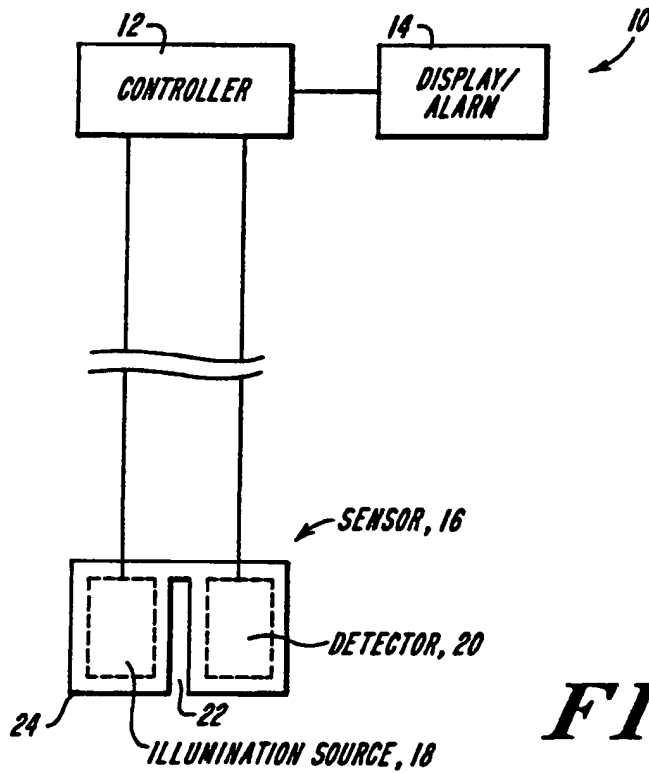


FIG. 1

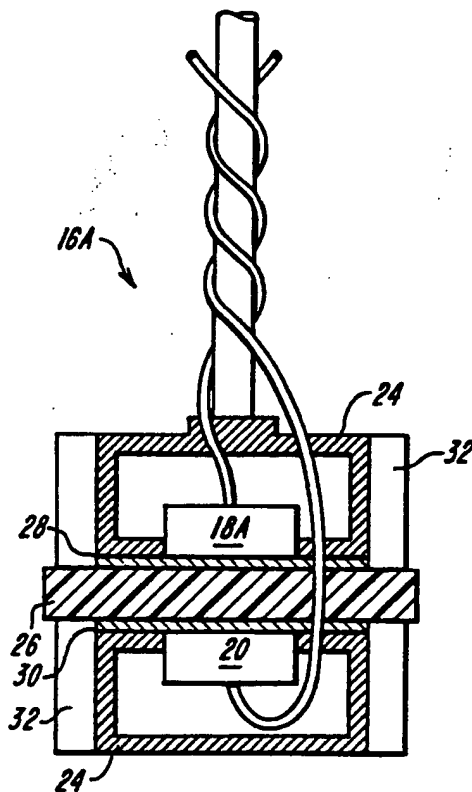


FIG. 2

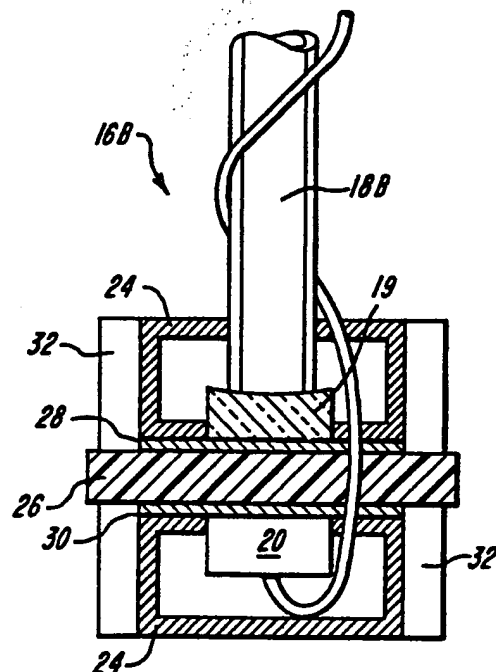
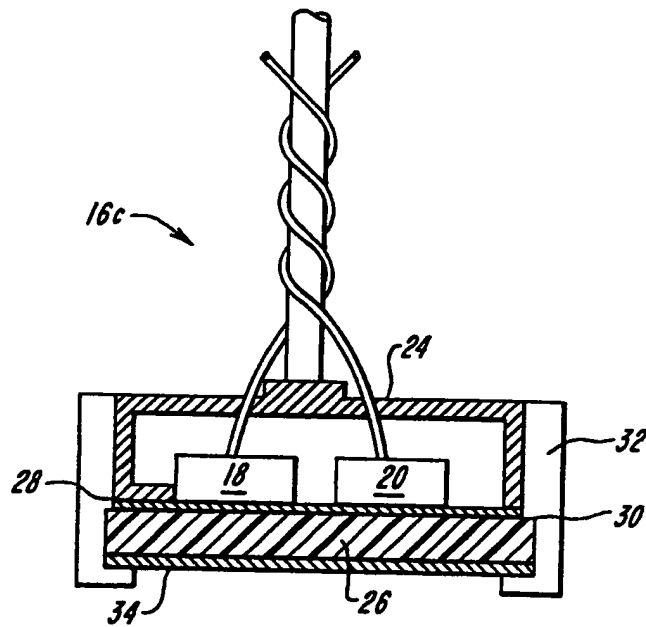
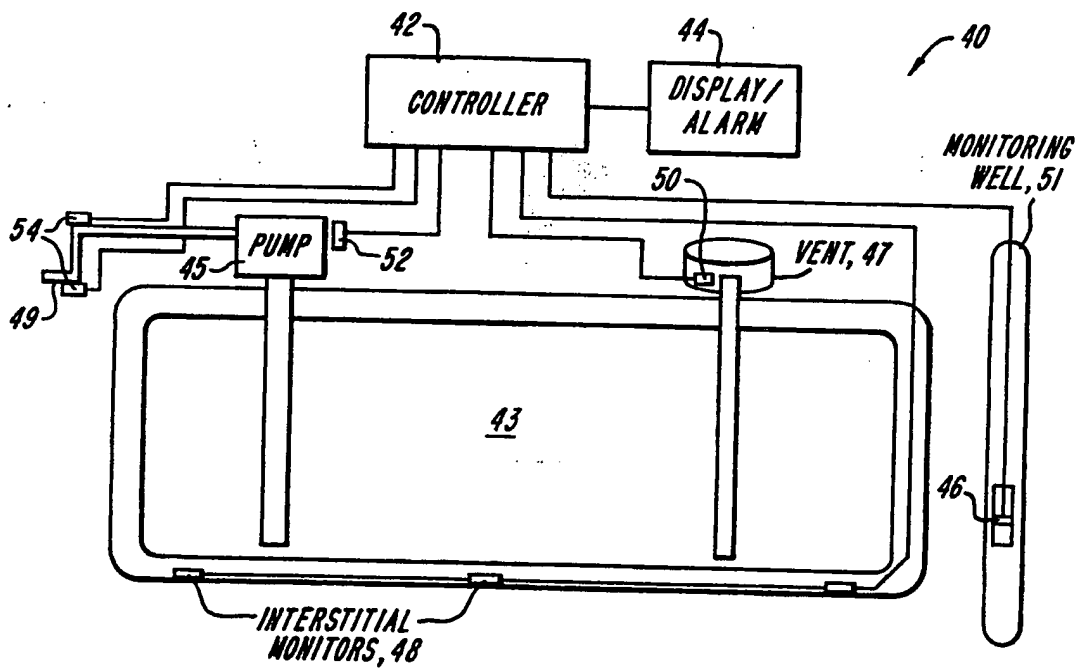
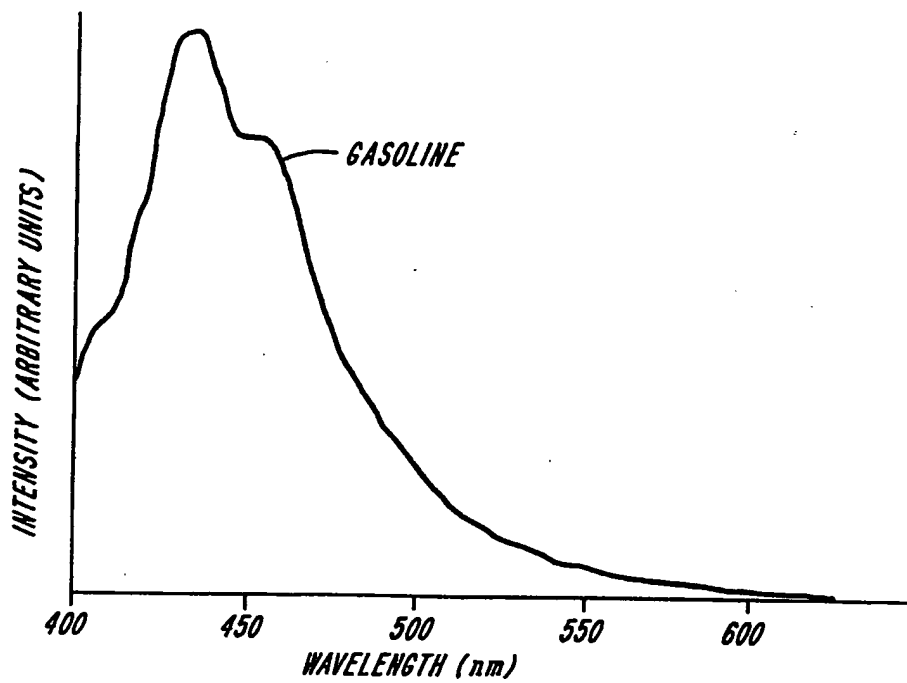
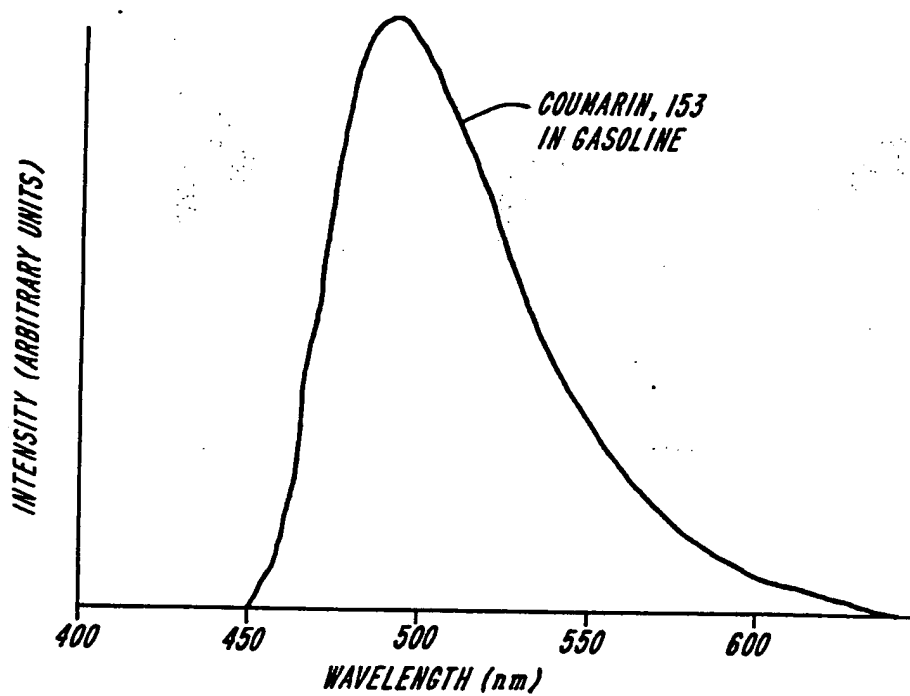


FIG. 3

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**FIG. 4****FIG. 5**

3/3

**FIG. 6****FIG. 7**

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/07480

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
Int.Cl. 5 G01N21/64

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

G01M ; G01N

Documentation Searched other than Minimum Documentation
to the extent that such Documents are included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,1 313 131 (INTERNATIONAL COMBUSTION LIMITED) 11 April 1973 see page 1, line 60 - line 63; claims 3-5	1-4
X	US,A,3 061 723 (S.F.KAPFF) 30 October 1962 see claims 1-5	1,5,6
X	US,A,2 593 391 (E.E.BRAY) 15 April 1952 see claim 1	1
X	GB,A,2 142 955 (NL PETROLEUM SERVICES LIMITED) 30 January 1985 see claims 1,11	1
Y	US,A,4 897 551 (M.G.GERSH ET AL.) 30 January 1990 see claims 1-21	17,18

¹⁰ Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

12 FEBRUARY 1992

Date of Mailing of this International Search Report

24 FEB 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

VAN DEN BULCKE E.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	US,A,4 709 577 (G.M.THOMPSON) 1 December 1987 see claims 1-12 ---	17,18
A	US,A,3 842 270 (M.D.GREGORY) 15 October 1974 see claim 1 ---	1
A	FR,A,913 790 (R.H.FASH) 3 June 1946 ---	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9107480
SA 53106**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-1313131	11-04-73	None	
US-A-3061723		None	
US-A-2593391		None	
GB-A-2142955	30-01-85	AU-A- 2791584	10-01-85
		CA-A- 1221847	19-05-87
		DE-A- 3418587	17-01-85
		FR-A- 2556465	14-06-85
		NL-A- 8401584	01-02-85
		SE-A- 8402695	07-01-85
		US-A- 4609821	02-09-86
US-A-4897551	30-01-90	None	
US-A-4709577	01-12-87	None	
US-A-3842270	15-10-74	CA-A- 1006710	15-03-77
		DE-A- 2446594	30-04-75
		FR-A, B 2249326	23-05-75
		JP-A- 50075485	20-06-75
FR-A-913790		None	